Geochemical Investigations of Volcanoes in Japan. XXXII. Residual Magmatic Waters in Cavities of Trachyandesitic Basalt in Imari District, Saga Prefecture, Japan*

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Introduction

It is of high importance to understand the nature of water and other volatile components in magmas for the study of many important phenomena such as the nature of the primary hot springs, the primary atmosphere, the primary hydrosphere, magmatic differentiation, ore deposits, etc. But our knowledge of the nature of the magmatic substances is very scanty. Although many reports1) related to the magmatic water have been published, the most part of these works is only the survey of the nature of the magmatic waters and gases. There have been only a few reports2) on the relation between the real magmatic waters and these geochemical phenomena from the geochemical point of view.

In the previous paper3) one of the present authors (Iwasaki) has given the definition of the real magmatic state that we can see on the surface of the Earth's crust, and in the present paper this definition described in the following paragraph was also adopted.

The real magmatic state near the surface of the Earth's crust can be defined as natural molten state of the rock-forming material such as molten lavas at lava lake of Volcano Kilauea in Hawaii and Volcano Mihara, Oo-sima, Idu in Japan3). Substances derived directly from these rock-forming materials in the real magmatic state can be called the magmetic substances, and the waters derived directly from these magmatic substances can be also called the magmatic waters. By this definition, the waters contained in these natural rock-forming minerals of igneous rocks are no doubt magmatic, but all of them are not always juvenile, because the molten rock-forming material may come from the resulting substances, some of which can be already solidified on the surface of the Earth before the introduction of them into the magmatic chemical system by remelting, assimilation or migmatization.

According to the theory of the magmatic

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* XXXI; *J. Chem. Soc. Japan*, **76**, 1116 (1955).

1) H. Davy, *Phil. Trans.*, II, 367 (1822); *Ann, Chim. et Phys.*, **21**, 132 (1822); D. Brewster, *Trans. Roy. Soc. Edinburgh*, **10**, 1 (1826); R.T. Simmler, Pogg. *Ann.*, **105**, 460 (1858); H.C. Sorby, *Geol. Soc. London Quart. Journ.*, **14**, 453 (1858); A.W. Wright, *Am. J. Sci.*, **21**, 209 (1881); W. Ramsay, *Proc. Roy. Soc.*, **58**, 65 (1895); A. Gautier, *Compt. rend.*, **132**, 58, 189 (1901); *Econ. Geol.*, **1**, 688 (1906); R.T. Chemberlin, "The Gases in Rocks", (1908); A. Brun, "Recherches sur L'Exhalaison Volcanique", (1911); A. L. Day and E. S. Shepherd, *Bull. Geol. Soc. Am.*, **24**, 573 (1913); E.S. Shepherd, *Am. J. Sci.*, **35** A, 311 (1938); J. Jaggar, ibid., **238**, 313 (1940); E.F. Holden, *Am. Mineralogist*, **10**, 203 (1925); W.H. Newhous, *Econ. Geol.*, **27**, 419 (1932); **28**, 744 (1933); S.T. Yuster, *Am. J. Sci.*, 5 ser. **31**, 363 (1936); E. Ingerson, *Am. Mineralogist*, **32**, 375 (1947); P.A. Peach, ibid., **34**, 413 (1949); H.S. Scott, *Econ. Geol.*, **43**, 637 (1948).

2) S. Tsuboi, K. Sugawara and S. Oana, *Science* (*Kagaku*), **14**, 102 (1944); K. Sugawara, S. Oana and T. Koyama, *Proc. Imp. Acad. Tokyo*, **20**, No. 10, 721 (1944); *Proc. Japan Acad.*, **25**, No. 3, 103 (1949).

3) I. Iwasaki, *Journ. of Geography* (Japan), **60**, 140 (1951).

differentiation by N. L. Bowen[4] and V. M. Goldschmidt[5], along with lowering of temperature fractional crystallizations of magmas take place with a separation of solids and mother liquors or residual magmas, and the aqueous magmatic solutions derived from the volatile components of magmas will remain when most of the parts of rock-forming silicate minerals have crystallized out from the magmas and the temperature of the residual magmas is lowered below the critical point of water (374.3°C, 217.7 atm.). These aqueous magmatic solutions which remained in the cavities of igneous rocks and rock-forming minerals as liquid inclusions, etc. can be called the residual magmatic water.

From these points of view the present authors have distinguished the magmatic waters obtained directly from the molten magmatic substances such as molten lavas from the residual magmatic waters which remained in the cavities of their mother igneous rocks and minerals. In the present paper some of the results obtained on the residual magmatic waters from trachyandesitic basalt in Imari district which has been found by K. Muta, Geological Institute, Faculty of Engineering, Kyushu University, in 1948, and the related problems are reported.

TABLE I

CHEMICAL COMPOSITION OF VOLCANIC ROCKS FROM IMARI DISTRICT, NAGAHAMA, HAMADA-SI, SIMANE PREFECTURE AND THE FUJI VOLCANIC ZONE

	Imari District				Hamada Nephline-basalt	Fuji Volcanic Zone	
	No. 1	No. 2	No. 3	No. 4			
SiO_2	48.87	50.46	54.90	56.17	34.98	49.60	54.66
TiO_2	1.24	2.12	1.94	1.00	2.39	1.40	1.10
Al_2O_3	16.00	18.41	17.38	16.83	11.18	16.96	17.91
Fe_2O_3	5.52	2.10	1.35	1.62	5.99	5.40	1.92
FeO	5.16	7.08	5.66	5.43	8.83	6.65	6.26
MnO	0.21	0.29	0.15	0.14	0.26	0.21	0.18
MgO	8.66	4.03	4.46	2.83	8.36	5.92	5.45
CaO	8.97	7.11	7.25	6.98	13.52	10.03	8.42
Na_2O	2.75	3.35	3.04	4.18	4.22	2.48	2.89
K_2O	0.86	1.28	0.84	1.17	3.99	0.58	0.42
H_2O	2.04	3.70	2.63	4.55	3.63	0.62	1.04
P_2O_5	n. d.	n. d.	n. d.	n. d.	2.53	0.20	0.10
S	n. d.	n. d.	n. d.	n. d.	0.10	n. d.	n. d.
Cl	0.015	n. d.	0.012	0.029	0.013	n. d.	0.010
Total	100.29	99.93	99.71	100.93	100.01	100.05	100.49

Occurrence and the Nature of Mother Rocks and their Cavities

The trachyandesitic basalts in question are distributed in hill country running close to the south of a railway-station of the Matuura-line, Kuhara, Saga Prefecture as shown in Fig. 1. These rocks have higher alkali contents than the volcanic rocks in the Fuji Volcanic Zone as will be seen in Table I, and lots of amygdaloidal cavities, some of which are filled with mineral substances mainly carbonate and silicate minerals; some are empty and some have mineral substances and aqueous solutions.

Fig. 1. Locality map.

According to Dr. H. Kuno, Geological Institute, Faculty of Science, Tokyo University, these trachyandesitic basalts have intergranular texture and holocrystalline structure, and a relatively small amount of phenocrysts (olivine, titaniferous augite, etc.) in the groundmass, in which labradorite, potash-andesine, olivine and augite are seen. And also in the druses of these rocks, calcite, aragonite, siderite and ankerite are seen.

These rocks show a remarkably heterogeneous appearance; for instance in some

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[4] N.L. Bowen., "The Evolution of the Igneous Rocks", (1928).

[5] V.M. Goldschmidt, *Z. Elektrochem.*, 28, 411 (1922).

parts of the mother rocks many cavities are clustered, but few cavities in the other parts. The size of these cavities varies from extremely small to about 10 cm. long, and these cavities are irregularly distributed in their mother rocks. There seems to be no remarkable regularity among their distribution of their sizes, number and inclusions (minerals, solutions and gases). The nature of these cavities in their mother rocks from Imari district closely resembles that of nepheline-basalts from Nagahama, Hamada-si Simane Prefecture, but there are some distinct differences between the properties of these two volcanic rocks. The cavities of nepheline-basalt are lined by zeolite (often bearing a smaller amount of calcite crystals), and the great part of larger cavities have irregularly angular form. On the other hand the forms of the cavities in trachyandesitic basalts are smoothly amygdaloidal, and in them the carbonate minerals such as calcite, aragonite and siderite are remarkably abundant. From the facts mentioned above, it seems that the rocks in Imari district have not been subjected to so large a pressure that their amygdaloidal cavities had changed their forms during their solidification as in the case of nepheline-basalt from Nagahama district, and are, therefore, more suitable to be used in the study of the nature of the magmatic substances.

The locations from which the samples for the chemical analysis were collected, are also shown in Fig. 1. The chemical compositions of the minerals co-existing with magmatic waters in the cavities are also shown in Table II. For example, one of the modes of occurence of these minerals is shown in Fig. 2. The number in Fig. 2. is the same as Table II.

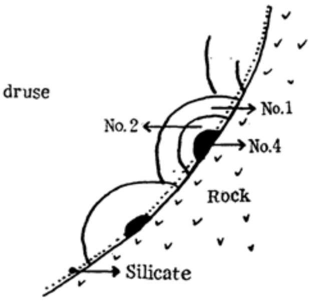

Fig. 2. The mode of occurrence of these minerals in the cavities of rocks.

Chemical Composition of the Residual Magmatic Solutions

Although it has already been found by Sugawara et al.[2] that each chemical composition of the inclusion waters from various cavities in nepheline-basalt in Hamada district varies remarkably each others, we are obliged to study the mixed sample from several cavities, because we cannot collect a sufficient amount of waters from only a single cavity for the complete chemical analysis on account of the nature of their occurrence. But some of the ingredients of these solutions, such as pH, Cl^-, NO_3^-, NO_2^-, NH_4^+, are determined for each cavity as shown in Table III.

As pH values in Table III were measured by pH test paper (B. T. B.), these values are not exact as already mentioned in the previous papers[6], but we can guess the outline of the properties of the waters and their variation from these so-called pH values.

TABLE II

CHEMICAL COMPOSITIONS OF THE MINERALS IN THESE CAVITIES

	Calcite ⟷ Siderite					Silicate	
CO_2	42.57	41.82	26.43	38.88	35.63	—	—
CaO	50.47	49.58	33.84	14.58	1.28	1.82	1.33
MgO	1.17	1.71	2.57	5.84	1.43	11.18	14.15
FeO	2.56	3.83	22.28	36.23	58.19	1.88	2.39
Fe_2O_3	0.31	1.44	2.33	3.06	1.41	14.93	13.26
MnO	1.68	1.47	7.05	0.73	0.76	0.32	0.62
SiO_2	—	—	2.52	—	—	41.02	44.13
Al_2O_3	—	—	1.76	0.38	0.51	2.89	0.60
H_2O (−)	—	—	—	—	—	20.53	18.04
H_2O (+)	—	—	—	—	—	6.19	5.63
P_2O_5	—	—	—	—	—	0.12	0.06
Cl	—	—	—	—	—	0.002	0.002
Total	98.76	99.85	98.78	99.70	99.21	100.88	100.21

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6) I. Iwasaki, "Geochemistry", in "Chemical Experiments", (1941) II, Vol. 12, 1; I. Iwasaki, M. Ieyosi, *J. Chem. Soc. Japan*, **64**, 1456 (1943); I. Iwasaki, *Japan Analyst*, **1**, 175 (1952).

TABLE III

CHEMICAL COMPOSITION OF THE RESIDUAL MAGMATIC WATER IN THE CAVITIES OF TRACHYANDESITIC BASALT FROM IMARI DISTRICT

Sample	Date of sampling		Location	Amount collected (g.)	pH	Cl (mg./l.)	NH$_4$ (mg./l.)	NO$_2$ (mg./l.)	NO$_3$ (mg./l.)
M	Aug.	1948	Kusuku	0.4594	—	76	71.2	—	—
A1	Mar.	1949	〃	—	7.0	—	—	—	—
A2	〃	〃	〃	—	6.6	—	—	—	—
A3	〃	〃	〃	0.4789	6.9	7.2	40.5	0.8	0.2
A4	〃	〃	〃	0.4135	6.7	5.8	61.6	0.4	0.4
A6	〃	〃	〃	—	6.4	—	—	—	—
A8	〃	〃	〃	—	6.6	—	—	—	—
1	Oct.	1949	Kuhara	—	6.6	—	—	—	—
2	〃	〃	〃	—	6.8	—	—	—	—
3	〃	〃	〃	0.3934	6.8	9.0	66.7	0.3	0.3
4	〃	〃	〃		6.8				
B1a	〃	〃	Kusuku	0.8209	6.0	29.2	11.4	0.4	0.2
B1b	〃	〃	〃	1.1465	〃	12.5	15.9	0.2	0.6
B1c	〃	〃	〃	0.1896	〃	4.0	72.2	0.3	1.7
B2	〃	〃	〃	0.5834	〃	6.2	10.0	0.2	0.7
B3a	〃	〃	〃	0.9982	〃	7.2	10.1	0.7	0.2
B3b	〃	〃	〃	0.9455	〃	6.6	17.1	0.3	0.3
B3c	〃	〃	〃	1.4472	〃	9.8	4.7	0.04	0.2
River water	〃	〃	〃	—	6.8	3.7	0.8	0.8	—
K	Nov.	1950	〃	100 cc.	7.0	10.1	0.63	0.005	0.033
River water	〃	〃	〃	—	6.7	9.1	0.096	0.000	0.030

TABLE IV

CHEMICAL COMPOSITION OF NATURAL WATERS FROM VARIOUS ORIGINS

	Residual magmatic waters				
	Imari (mg./l.) (K)	Hamada (mg./l.) (1)	Hamada (mg./l.) (2)	River water Imari (mg./l.)	Sea water^{+} (mg./kg.)
pH	7.0	5.6	3.6	6.7	7.5–8.8
Evaporation residue	280	—	—	—	35,500
Na	30.2	139	491	48.4	10,600
K	29.0	—	120	9.0	380
Ca	126	76	112	10.2	400
Mg	0.0	22	11	0.0	1,300
Fe	0.67	4.1	2.3	0.64	0.002
Al	<0.6	11.	16	<0.6	0.1
NH$_4$	0.8	0.08	14	0.096	—
Cl	10.1	170	732	9.1	19,000
SO$_4$	4.2	173	326	3.0	2,600^{++}
NO$_3$	0.033	4.4	97	0.030	—
NO$_2$	0.005	21	0.54	0.000	—
SiO$_3$	—	35	28	—	—

$^{+}$ V.M. Goldschmidt, "Geochemistry", (1954) p. 49.

$^{++}$ Calculated from S=880 mg./kg.

pH values vary from about 6.0 to about 7.2, and the tendency of going to the alkaline side of these values after collection of samples from the mother rocks for location B is perhaps due to the fact that dissolved carbon dioxide escapes from the sample waters when they are exposed to the atmosphere, in which carbon dioxide content is very small as 0.03% (vol.), by crushing the mother rocks. This fact indicates that the waters in the cavities are almost neutral or slightly acidic and absence of the extremely acidic and basic substances, so far as the data tell. And also this fact will easily be understood if they have already reacted completely with the substance around the cavities and have already attained nearly completely to the equilibrium between them. This nature is quite different from that of the residual magmatic waters in rocks from Hamada district where acidic (pH 3.6; 5.6) and alkaline (pH 8.1) waters were found.

Chlorine content of these waters (4.0–29.2 mg./l.) is very small compared with that (25–1220 mg./l.) of the waters from Hamada district and comparable with that of the river waters near the mother rocks in this district as will be seen in Table IV.

On the contrary, NH_4^+ content of the waters in this district ranging from 0.63 to 66.7 mg./l. seems as a whole to be remarkably higher than that of the waters in Hamada district and the river waters described above.

NO_3^- and NO_2^- content of these waters ranging from 0.005 to 0.8 mg./l. and 0.033 to 1.7 mg./l. respectively are very small compared with that (4.4–97; 0.54–21 mg./l.) of the waters in Hamada district as the case of chlorine content.

As will be seen in Table IV, the concentrations of the other components such as Na, K, Mg, Fe, Al, SO_4, in these waters are remarkably lower than that of the waters from Hamada district. But only the calcium content of these waters is very high compared with that of the other components, and comparable with that of the waters from Hamada district. This nature is also quite different from that of the waters from Hamada district and sea water. It seems to be the corresponding nature that calcium carbonate minerals are very abundant in the cavities of the mother rocks in Imari district.

As will be seen in Tables III and IV, the variation in the chemical compositions of the inclusion waters from each cavity is quite remarkable like that recognized in Hamada district. Consequently we can conclude that these volatile components of magmas are not always collected uniformly in each cavity during the fractional crystallization of magmas depending on their geological environments and the nature of magmas and volatile components. This fact is also recognized from the irregular distribution of the cavities; their inclusions and minerals in their cavities as described above.

Discussion

a) Real Magmatic Waters.—The real magmatic waters defined above have already been obtained from lava lake at Volcano Kilauea in Hawaii by A. L. Day and E. S. Shepherd¹⁾, and at Volcano Mihara, Oo-sima, Idu in Japan by the present authors³⁾. In the magmatic waters from lava lake at Volcano Kilauea, a large amounts of many volatile components, such as Na, K, Ca, Fe, Al, Cl, F, Ti, S, are determined together with many volcanic gases such as CO_2, CO, H_2, SO_2. Afterward these results have been confirmed by Shepherd¹⁾ and J. Jaggar¹⁾ in lava lake at Volcano Kilauea and Mauna Loa in Hawaii. From these results we can conclude that all these magmatic waters obtained from lava lakes in Hawaii are of acidic nature. The magmatic waters obtained from lava lake at Volcano Mihara are also strongly acidic as will be seen in Table V.

TABLE V

CHEMICAL COMPOSITION OF THE MAGMATIC WATER OBTAINED FROM LAVA LAKE AT VOLCANO MIHARA, OO-SIMA, IDU, JAPAN

Sample: April 1, 1950.

Acidity	1.4 N
Cl	67.6 g./l.
Total S	0.16 〃
Si	0. 〃
Fe	69.8* 〃
Ca	0. 〃
Mg	0. 〃
Ti	0. 〃
Al	(trace) ?

* Mixed with iron chloride derived from iron tube.

As the temperature of molten lavas in these active lava lakes mentioned above is as high as about 1100°C, a remarkable distillation of the volatile matters in lavas is thought to take place. As a result, many volatile components of magmas (volcanic sublimates) issued in the volcanic gases are dissolved in distillates, magmatic waters, and some of them are hydrolyzed, and these magmatic waters acquire an acidic nature. These facts are already demonstrated by laboratory experiments. For example, when the mixture of sodium chloride and quartz powder is heated with water at about 1000°C, a large amount of hydrogen chloride is distillated with water⁷⁾. Thus, we can understand easily that these magmatic waters have acidic nature, but the chemical composition of these real magmatic waters from different volcanoes, and the same volcano at different times and also different parts of the same lava lake of one volcano at the same time are evidently very dissimilar in appearance depending on the nature of the magmas, especially the surface of the magmas as that volcanic gases in lava lake at Volcano

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7) For example, R. Kiyoura and Y. Ito, *J. Ceram. Assoc. Japan*, **60**, 325 (1952).

Kilauea[1) and Volcano Mihara[3,8).

When these magmatic waters spring out directly on the surface of the Earth's crust, they form the primary hot springs, which are consequently of acidic nature, and are thought to be distributed usually in the vicinity of volcanic active centers. On the other hand, when these magmatic gases and waters remain in the cavities of the mother rocks, the acidity of these solutions is decreased gradually by the reactions, with their country rocks either before or after the condensation of these volatile magmatic components into aqueous solutions. Consequently it will easily be understood that all these residual magmatic solutions in the cavities of their mother rocks as found in Hamada and Imari districts are almost all neutral or slightly acidic or slightly alkaline in nature as described above. And when these reactions with their country rocks proceed still more, these waters must gradually become alkaline in nature depending on their nature. And also it will easily be understood that there are many kinds of chemical compositions of magmatic waters depending on time elapsed after separation from their magmas, and the nature of their mother magmas and volatile components and chemical reactions with their country rocks after separation from their magmas.

b) Primary Hot Springs.—The primary hot springs distributed in the vicinity of active volcanic craters as described above are usually of acidic nature. But, needless to say, there are many acidic hot and cold (mineral) springs in the world which are distributed in various places where no relations with volcanic activity can be seen, or in the special places where oxidation process by oxygen in the atmosphere easily takes place owing to the special geological conditions. These acidic mineral springs have usually a characteristically large amount of sulphate ion compared with the other hot springs as already shown in the hot springs of Japan by the present authors[9), and their acidity is thought to be due to the existence of a large quantity of sulphuric acid formed by the oxidation of sulphur compounds in these springs by the atmospheric oxygen near the surface of the Earth's crust (Table VII). Considering these facts, these acidic mineral springs are thought to be of secondary origin[10). Thus, the primary hot springs of acidic nature are distinguished from these cold acidic mineral springs of secondary origin. Some of these primary hot springs formed by condensation of the volatile components of magmas after the separation from their magmas are easily distinguished from the other hot springs by means of determination of distribution of radioactive components such as radon and thoron between a gas phase and an aqueous phase as already reported in the previous papers[11). In these primary hot springs Rn and Tn are distributed in a gas phase in excess of the equilibrium content which is calculated on the basis of partition law between a gas phase and an aqueous phase. On the contrary, in the ordinary hot springs Rn or Tn are distributed usually in an aqueous phase in excess.

When these primary acidic hot springs react for a long time with their country rocks and the other substances around their ways to the surface of the Earth's crust the properties of these hot springs will gradually change, and in the end become of alkaline nature as the residual magmatic solutions in the cavities of volcanic rocks in Hamada and Imari district. If all alkaline hot springs are thus formed from these primary acidic hot springs, the alkaline hot springs are of course of secondary nature. But on the other hand, it is well known that alkaline aqueous solutions can be derived directly from the residual magmatic solutions as in the cavities of volcanic rocks in Hamada and Imari district. When these alkaline aqueous solutions spring out directly on the surface of the Earth's crust, they also form the primary alkaline hot springs. Consequently, it will easily be understood that there are two kinds of alkaline hot springs (primary and secondary in this sense), but they cannot yet be distinguished from each other by observations. When the springs which contain the magmatic substances are genetically called hot springs as is done by Allen and Day[12,10) the hot springs must have various kinds of chemical compositions and temperature depending on the nature of their geological environments, and the chemical compositions of the magmatic and meteoric substance introduced into the chemical system of hot springs. On the other hand it has been found by T. Terada[13) that hot springs which have no relations to volcanic activities are

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8) I. Iwasaki, H. Shimojima and M. Tsuda, *Mass Spectroscopy*, No. 1, 52 (1953); No. 4, 39 (1955).

9) I. Iwasaki, *J. Chem. Soc. Japan*, **56**, 1427 (1935); *J. Balneol., Soc. Japan*, Vol. I, No. 3 and 4, 106 (1942).

10) E.T. Allen and A.L. Day, "Hot Springs of the Yellowstone National Park", (1935) p. 39.

11) I. Iwasaki, T. Katsura, H. Shimojima and M. Kamada, "Radioactivity of volcanic gases in Japan", Bull. Volcanologique, in press.

12) E.T. Allen, *Econ. Geol.*, 30, 1 (1935); A.L. Day, *Bull. Geol. Soc. Am.*, 50, 317 (1939).

13) T. Terada, *Bull. Earthq. Res. Ins.*, 8, 377 (1930).

formed by the heat produced by crustal movements. Considering these facts, we cannot distinguish the hot springs of magmatic origin from the other mineral springs only by their chemical compositions and temperature of their waters, because we have no method to distinguish the magmatic substances from the others. These facts give the basis to the genetical definition of hot springs reported in the previous papers[14] that hot springs can be defined genetically as the springs which contain more or less magmatic substances regardless of their chemical compositions and temperatures.

c) **Primary Hydrosphere and Primary Atmosphere.**—The nature of the primary hydrosphere and the primary atmosphere are largely conditioned by the mode of origin of the Earth. There have been many reports on the origin and formation of the Earth, but up to the present, we cannot understand completely yet the chemical processes of the formation of the Earth without any serious objection. The formation of the hydrosphere starts with the condensation of water vapour. On the geochemical processes of the formation of the primary atmosphere and the primary hydrosphere, there are distinct differences between Goldschmidt's theory[15] and the accretion theory[16] developed recently. According to Goldschmidt, the primary atmosphere and the primary hydrosphere are mainly formed by the condensation of the original atmosphere, which was formed at the first stage of the geochemical distribution of the chemical elements in the Earth, and they have increased unceasingly by addition of volcanic gases during the long geologic time. On the other hand, according to the accretion theory the primary atmosphere and the primary hydrosphere are thought to be mainly formed gradually from the volcanic gases expelled by heating from the cold original Earth material.

But in all cases, it has been shown that the volcanic gases occupy the important part of the formation of both the atmosphere and the hydrosphere. From these points of view, it seems to be able to estimate the nature of the primary hydrosphere and the primary hydrosphere from the properties of the volatile magmatic substances, especially the magmatic waters and volcanic gases. As already reported in the previous paper[17], water, nitrogen and carbon dioxide expelled from volcanic rocks by heating have larger contents in the gases expelled at relatively lower temperature (up to about 500°C) than in that expelled at high temperature (800–1200°C). And also we can detect many halogen and sulphur compounds in the volcanic gases from lava lakes and fumaroles of high temperature, but cannot detect any halogen compounds in the volcanic gases from fumaroles of low temperature. Although sulphur compounds such as hydrogen sulphide are detected in many fumarolic gases of low temperature, the main components of these fumaroles are usually nitrogen, carbon dioxide and water vapour. From these model experiments descibed above[17] and the nature of the volcanic gases, by accretion theory we can guess that during the period of relatively low temperature up to about 500°C the contents of sulphur and halogen compounds in atomsophere and hydrosphere should be very small, but when the temperature reached above about 800°C, sulphur and halogen compounds are abundantly expelled from the original Earth material, and consequently the hydrosphere condensed from these volcanic gases will have more sulphur and halogen compounds. In the initial stage of the formation of the hydrosphere, its acidity would increase by the addition of hot acidic rain waters[18] condensed from the volcanic gases of high temperature until active chemical reactions with country rocks which occurred in hydrosphere used up these acids supplied by these volcanic gases. Then the acidity of the hydrosphere would decrease gradually to that of the present hydrosphere (Table IV). The chemical nature of the hot acidic rain waters will be able to be estimated from magmatic waters as will be seen in Table V, and the waters condensed from fumaloric gases. And the chemical properties

TABLE VI

CHEMICAL COMPOSITION OF THE RESIDUAL MAGMATIC GASES IN THE NEPHELINE-BASALT IN HAMADA DISTRICT

Dissolved gases in the inclusion.

	No. 13	No. 19
O_2	0.00 cc./l.	0.00 cc./l.
N_2	6.32 〃	13.54 〃
CO_2	2.25 〃	1.23 〃
H_2	0.00 〃	0.00 〃
CH_4	0.00 〃	0.00 〃
Tension of nitrogen gas	0.366 atm.	0.795 atm.

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[14] I. Iwasaki, *J. Chem. Soc. Japan*, **56**, 252 (1935).

[15] V. M. Goldschmidt, *Z. Elektrochem.*, **28**, 411 (1922); "Geochemistry", (1954) p. 11.

[16] H.O. Urey, *Geochim. et Cosmochim. Acta*, **1**, 209 (1951); 263 (1952).

[17] I. Iwasaki, T. Katsura and N. Sakato, *J. Chem. Soc. Japan*, **76**, 778 (1955).

[18] I. Iwasaki, "Introduction to Geochemistry", (1953) p. 206; I. Iwasaki, T. Nitta and T. Tarutani, *J. Chem. Soc. Japan*, **74**, 1003 (1953).

of the primary atmosphere will also be able to be estimated from the chemical compositions of the residual magmatic gases and volcanic gases from various volcanoes[1,3,8] and various kinds of volcanic rocks[1,17,19]. Chemical compositions of the residual magmatic gases in the nepheline-basalt in Hamada district reported by Sugawara et al[2] are shown in Table VI.

From these volcanic gases we can completely understand that there is no free oxygen in the primary atmosphere. This fact is in good aggreement with the nature of the original atmosphere by Goldschmidt[15].

The primary hydrosphere formed by condensation of the original atmosphere by Goldschmidt must also be acidic nature owing to the dissolution of volcanic exhalation by the violent volcanic action as in the case of the accretion theory. In all cases, the acidic nature of the primary hydrosphere is derived from volcanic exhalations and by unceasing reactions with the country rocks, its acidity would decrease until it became equal that of the present hydrosphere. The chemical nature of the primary hydrosphere at the initial stage, especially primary ocean, seems to be able to be estimated from the chemical composition of hot river waters which are formed by the condensation of the volcanic gases and by running on the hot volcanic rocks erupted recently[18]. After violent chemical reactions with country rocks the nature of the hydrosphere seems to resemble that of the residual magmatic waters and the hot springs. The average contents of main components, such as Cl, SO_4, HCO_3, Na, Ca, Mg, of the hot springs in Japan calculated by the present author[9] are shown in Table VII.

From these points of view, it seems that the content of carbon dioxide in the primary atmosphere is larger than that of the present atmosphere, and the salt content of the primary ocean is about one-tenth that of the present hydrosphere.

d) Magmatic Substances in the Cavities.—As already shown in the description of the nature of the mother rocks and their cavities in this paper, these rocks and the distribution of cavities show remarkably heterogeneous appearance from one part to another. There seem to be no remarkable regularities among their distribution and the nature of their cavities (sizes, inclusions, such as minerals, solutions and gases). Some of the cavities are empty (only filled with gases); on the other hand, some of them are completely filled with mineral substances, mainly carbonates and silica and silicate minerals, and some of them hold mineral substances and aqueous solution in addition to the residual gases. From the nature of these cavities it might be safely concluded that these mineral materials, waters and gases, are easily mobile in the mother rocks at the stage of the formation of these cavities. If these characteristics are excluded, it seems to be impossible to understand the fact that some of these cavities are completely filled with the mineral substances or are empty. From this point of view, the computation of the concentration of the inclusion water before the minerals, lining the cavity-wall, separated was carried out by K. Sugawara et al.[2], and they showed that the concentration is very high (280.88 g./l.); that is, 3.65 times higher than the Japanese record of hot spring salinity, 77.1 g./l. of Arima-shin-onsen.

TABLE VII

AVERAGE CONTENTS OF MAIN COMPONENTS OF THE HOT SPRINGS IN JAPAN

	Number of sample	Salt content (g./kg.)	Na (g./kg.)	Ca (g./kg.)	Mg (g./kg.)	Cl (g./kg.)	SO_4 (g./kg.)	HCO_3 (g./kg.)
Acidic "hot spring" (>25°C)	63	2.21	0.305	0.195	0.0537	0.787	1.51	0.257
Acidic mineral spring (<25°C)	162	6.09	0.692	0.210	0.0833	1.07	4.51	0.547
Neutral "hot spring" (>25°C)	25	2.76	0.631	0.247	0.0199	1.01	0.472	0.321
Neutral mineral spring (<25°C)	23	4.08	0.873	0.438	0.0829	1.98	0.471	0.532
Alkaline "hot spring" (>25°C)	331	2.19	0.534	0.192	0.0198	0.847	0.349	0.246
Alkaline mineral spring (<25°C)	108	6.78	2.06	0.300	0.107	3.20	0.337	1.34
Total hot spring	712	3.86	0.768	0.221	0.0557	1.25	1.70	0.491

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19) E.S. Shepherd, *J. Geol.*, 33, 289 (1925); E.S. Shepherd and H.E. Merwin, *J. Geol.*, 35, 97 (1927).

Conclusion

From the definition of the real magmatic state, many kinds of the magmatic waters should be formed even from the same magma depending on their geological environments. The residual magmatic water described above can be distinguished from the magmatic waters derived directly from the molten lavas. The magmatic waters are acidic on account of dissolution of volatile magmatic components, but the residual magmatic waters must be usually neutral, slightly alkaline or acidic owing to the chemical reactions with their country rocks. These magmatic waters are not always juvenile, and their temperature, salt contents and chemical composition must cover a wide range. Consequently these magmatic waters cannot be distinguished distinctly from the ordinary natural waters by means of their temperature and chemical compositions.

When the hot springs are defined as the springs which contain the magmatic waters, many kinds of springs should be formed owing to the mechanism of the formation of hot springs. Even the primary hot springs derived directly from the magmatic waters have also a wide variety. For example, the acidic primary hot springs formed directly from the magmatic waters can be changed gradually into the alkaline hot springs by the reactions with their country rocks and the introduction of the other substances. On the other hand, the primary alkaline hot springs can also be formed directly from the residual magmatic waters.

From the nature of the magmatic waters and volcanic gases, the chemical nature of the primary hydrosphere and the primary atmosphere in their initial stage can be estimated. The primary hydrosphere must be acidic on account of the hot acidic rain waters at first, and change gradually into alkaline nature by the reactions with their country rocks and the other substances introduced by river waters. The primary atmosphere has no free oxygen, but has larger carbon dioxide content than the present atmosphere.

From these facts that all the cavities of the mother rocks in question have a quite distinct boundary and the distribution of the magmatic substances in these cavities are quite dissimilar, it also might be safely concluded that these mineral substances must be easily mobile in the initial stage of the formation of these cavities. The problems on the mechanism of this surprising concentration of these mineral materials into the small cavities will be answered by the geochemical investigations in future.

Summary

1) The nature of the residual magmatic waters in the cavities of the trachyandesitic basalt in Imari district is described with the nature of their mother rocks and druse minerals.

2) From the definition of the real magmatic state, temperature, and chemical properties of many kinds of magmatic waters are discussed, and the residual magmatic waters are distinguished from the magmatic waters derived directly from lava lakes. It is concluded that the magmatic waters are not always juvenile.

3) The formation of the various kinds of the primary hot springs are discussed from the definition of hot springs and the various kinds of the magmatic waters.

4) Chemical nature of the primary hydrosphere and the primary atmosphere in the initial stage of their formation are discussed from the chemical properties of the magmatic waters and volcanic gases.

5) The important properties of the magmatic substances in the cavities of the volcanic rocks are discussed from the standpoint of the distribution of the magmatic substances in the cavities.

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